The University of Chicago

The Course of the Reaction between Manganese Dioxide, Potassium Hydroxide and Oxygen and the Manufacture of Potassium Manganate.

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL
OF SCIENCE IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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THE COURSE OF THE REACTION BETWEEN MANGANESE DIOXIDE, POTASSIUM HYDROXIDE, AND OXYGEN AND THE MANUFACTURE OF POTASSIUM PERMANGANATE

Among the important chemicals which in the past have been imported at so low a price that American manufacturers had not, up to the time of the European war, undertaken its production to any large extent is potassium permanganate. The obvious need for the product and its extreme scarcity have, however, made its manufacture in this country a necessity, and a number of plants are now engaged in producing it. Some of them encountered certain difficulties when they began continuous operation and at the suggestion of Professor Schlesinger I undertook to investigate the matter. Out of this investigation a number of results of both scientific and practical interest have developed and of these the most important are reported in this paper.

There are several methods for manufacturing the permanganate; the most widely used is apparently the one in which potassium manganate is first prepared as an intermediary product by heating a mixture of potassium hydroxide and manganese dioxide in a current of air. The resulting mix is then extracted with water or a dilute solution of caustic potash and the solution of manganate thus obtained is converted into a solution of the permanganate. The methods employed for this latter step need not be discussed here as the research now to be reported deals only with the first step. It is necessary, however, to point out that in this second step a large proportion of the caustic combined in the first is again liberated either in a form in which it can be directly utilized or in which it can be used after suitable treatment, depending upon the process used for the second step. Furthermore, owing in part to the spontaneous decomposition of manganate and permanganate solutions, in part to manganese dioxide precipitated out in the second step and in part to the fact that the first step never results in complete interaction of the components, there is always a relatively large amount

of manganese dioxide left over from each treatment. It is therefore self-evident that economical working of the process not only requires as high a yield as possible of the manganate in the first step, but that it is also necessary that the neutralization of the residual and recovered manganese dioxide and potassium hydroxide must be highly successful. Difficulties have apparently been encountered in both of these phases of the process and we have therefore made a study of the factors which influence their successful carrying out.

The conversion of manganese dioxide into potassium manganate by heating it in a current of air with potassium hydroxide has been extensively investigated. The most recent and apparently the most thorough of these investigations are those of Askenasy and Klonowski[1] and of Sackur[2] and his associates. The researches of the two groups of investigators do not lead them to the same conclusion. While the first named seem to hold to the opinion that the reaction follows the course usually found in the text books, represented by the equation

$$4KOH + 2MnO_2 + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O.$$

Sackur concludes that potassium manganate is never formed in this way, but that the product obtained in the reaction is a "mangani-manganate" which can be represented by the formula, $2K_2MnO_3,3K_2MnO_4$, $3K_2O$. In this conclusion he is corroborated by the work of Auger[3] who obtained a compound of similar composition by heating potassium permanganate with excess of potassium hydroxide. If Sackur's conclusion is correct it is clear that the highest yield that could be obtained in the reaction in terms of the amount of manganese dioxide oxidized to the manganate stage could be only 60 per cent, since the remaining 40 per cent must always remain as manganite. In support of this consequence of his theory of the course of the reaction Sackur cites his own experiments which show a maximum yield of between 55 and 66 per cent, the results of Askenasy and Klonowski who obtained similar yields, and the statements, made personally to Sackur by German manufacturers, that a yield of 60 per cent was the maximum

[1] *Z. Elektrochem.*, **16** (1910), 104, 170.

[2] *Ber.*, **43** (1910), 381, 448; **44** (1911), 777; *Z. Elektrochem.*, **16** (1910), 649; **18** (1910), 718; *Z. anorg. Chem.*, **73** (1912), 101.

[3] *Compt. rend.*, **151**, 69.

attained in practice.[1] When we first undertook this investigation the manufacturers with whom we were coöperating were not obtaining yields as high as those demanded by Sackur's theory and we, therefore, attempted to determine the best conditions for duplicating his results. The outcome of this work has been to show that Sackur's theory of the reaction is incorrect, for we were able to obtain yields corresponding to a conversion of over 98 per cent of the manganese dioxide into the manganate by use of the methods of work and of the proportions of the reacting substances which are discussed below.

I—THE COURSE OF THE REACTION BETWEEN MANGANESE DIOXIDE, POTASSIUM HYDROXIDE AND OXYGEN

In our experiments we decided to follow the procedure of Askenasy and Klonowski.[2] This procedure consists, briefly stated, in mixing the finely ground ore with a concentrated solution of caustic potash, drying the mix in a current of air to such a consistency that when cool it can be well powdered and will no longer become soft on raising it to the higher temperatures to which it is next exposed, and finally heating this powdered material in a current of air in an apparatus in which the mix can be continually ground while being heated. This apparatus consisted of a rotating drum, fitted with iron ribs parallel with the axle and with openings for removing material for analysis. The drum was rotated in an iron housing and was heated by gas. The axle was hollow and broken in the middle of the drum. Through one end of the hollow axle preheated air was introduced and into the other end a thermocouple was loosely fitted. The charge, prepared as above, was placed in the drum and with it a fairly large number of $^3/_4$ in. steel balls. As the drum rotated slowly (20 r. p. m.) the balls were lifted by the ribs in the sides of the drum and dropped back on the material, thus pulverizing the latter thoroughly throughout the process. That this continuous pulverization, which is recommended by the authors named above, considerably improves the yield

[1] It will be noted that the highest yields obtained by Sackur are a little higher than permitted by his theory. Sackur gives an explanation of this which the work herein reported shows to be incorrect. Askenasy in one experiment obtained very much higher results than Sackur. The experiment, however, has not been cited in refutation of Sackur's criticism of Askenasy and it is, therefore, likely that the result was never confirmed.

[2] *Loc. cit.*, p. 175.

was corroborated by our own results, which need not be recounted here.[1] In only two particulars did we depart from the method of Askenasy and Klonowski. In the first place in making the mix we used ore and alkali in varying proportions as described below while they used mixtures containing approximately equal parts by weight only. In the second place we used a somewhat lower temperature, keeping our mixes in the rotators at about 450° C. In one minor matter we also departed from the older investigation referred to. The preliminary drying was carried out in an electrically-heated oven instead of over a free flame, but this was merely a matter of convenience in regulating the temperature at this stage and in avoiding too great a contamination with carbon dioxide, which is likely to occur when the heating is carried out over the free flame. The heat was so regulated in this part of the process that when the mix was completely dry its temperature remained in the neighborhood of 300° C.

The preliminary heating, while it results in the absorption of some oxygen and in some experiments to quite a large amount, is in general carried out merely to prepare the material for the treatment in the rotary kilns in which the chief absorption usually takes place. The mass was usually analyzed after the preliminary heating was completed and, after it was placed in the kilns, analysis was repeated every few hours until oxygen absorption seemed to cease. This could be done without cooling off the whole mass because material could be withdrawn from the cylinders through the openings mentioned. The method of analysis was that employed by Askenasy and Klonowski.

Before proceeding to the discussion of the final results of this part of the investigation one important detail must be taken up. In one of our earlier experiments a mix was heated in the rotary kiln, as described, first in an atmosphere of dry air and then in oxygen. The potassium manganate content in air rose to 54.6 per cent, which is about 60 per cent of the yield possible according to the equation given above. Further heating in air caused a slight lowering of the yield. In oxygen the content of manganate rose to 63 per cent, at which point absorption of oxygen came to an end. The mass was then treated with enough water so that the mixture could be well stirred. It

[1] See however, p. 17.

was then dried as described above and reheated in oxygen in the kilns at 450°. The manganate content now rose to 77.9 per cent and a repetition of this procedure finally raised it to 81 per cent, representing a yield of 92 per cent of the theoretical on the assumption that manganate and not mangani-manganate is the product obtained. Frequent repetitions of analogous experiments showed that it was the moistening with water which raised the final yields, as merely by this treatment and without the use of oxygen we have been able to reproduce these and higher yields. Two questions were raised by this result. In the first place it would seem as if manganate is not as sensitive to moisture as usually stated. To bear this out the following may be cited. Steam was passed over a product containing 78.6 per cent of potassium manganate for 20 min. while the mass was kept at 450°. At the end of this time the manganate content had fallen only to 76.8 per cent. In the second place there is a possibility that moisture is necessary to obtain the highest possible yields. It is to be noted that in the experiment cited above the absorption of oxygen from *dry air* stopped at about 60 per cent of the amount of manganate possible on the assumption that it is the product formed. This accords with Sackur's theory of the reaction. In a similar experiment the absorption of oxygen from *dry air* stopped at the same point. In two other experiments in which manganese dioxide from a different source was used the same thing was observed. But in a fifth experiment the content of manganate rose in dry air until a maximum yield of 87 per cent was reached without remoistening. On the other hand we find that if instead of using dry air we employ air that has been moistened by passing it through water there is much less likelihood that the reaction will stop before the maximum possible oxidation has been attained. The bearing which these results may perhaps have on the theory of the reaction will be taken up below; the experimental results have been introduced at this point to explain how the maximum yields reported in the next paragraph were obtained. Based on the results described above our procedure was invariably to allow absorption of oxygen to proceed as far as it would in air, then to remoisten and reheat the material in air, and finally to reheat in oxygen. The latter treatment seems merely to hasten the absorption of the last part of the oxygen and not to raise the yield above that which

could be reached in air if enough time and repeated remoistening were employed.[1]

The fact that a yield of nearly 100 per cent of the theoretical can be attained—a fact that is important because of its practical aspect and because it proves Sackur's theory of the course of the reaction incorrect—was discovered as the result of a series of experiments in which the relative amounts of manganese dioxide and of potassium hydroxide were varied within wide limits.[2] The experimental data of this series are given in Table I and are reproduced graphically in Fig. 1.

TABLE I—SHOWING THE INFLUENCE OF VARYING THE RELATIVE AMOUNTS OF POTASSIUM HYDROXIDE AND MANGANESE DIOXIDE ON THE YIELD OF MANGANATE

Ratio	1.20	1.55	2.11	2.28	2.43	2.49	2.62	2.79	3.12	3.62	4.21
Per cent K_2MnO_4	35.1	51.2	73.8	77.2	79.8	81.1	76.5	68.9	57.4	41.7	36.4
Per cent yield	29.5(*a*)	47.6(*a*)	79.4	86.4	95.0	98.4	94.3	87.8	75.5	61.0	57.9

(*a*) In the experiments in which 1.2 and 1.55 moles of potassium hydroxide, respectively, were used for each mole of manganese dioxide, there is not enough of the former to convert all of the manganese dioxide into manganate. If the yield is calculated on the basis of the amount of potassium hydroxide converted into manganate the results are 49.2 and 60.4 per cent, respectively.

In the table the first row gives the value of the ratio moles of potassium hydroxide to one mole of manganese dioxide; the second row, the final content of potassium manganate contained in the masses; and the third row, the per cent yield. The last set of data was obtained by determining for the final sample the content of potassium manganate and the total manganese,[3] and calculating what per cent the manganate found was of that possible if all of the manganese had been converted into manganate. In Fig. 1 the ratios mentioned above are plotted against the percentage yield.

Inspection of the table and the curves shows that the yield of manganate varies with the relative amount of caustic potash used. From the curve it can be seen that the percentage of manganese converted into manganate is directly proportional to the relative amount of the alkali since the curve representing the

[1] Askenasy and Klonowski (*Loc. cit.*, p. 111) describe one experiment in which they moistened the material from time to time with a few drops of water. They seem to lay no stress on this point and our experience is that a few drops of water would be quite ineffective. Attention may also be called here to the German Patent 266,347 (1912) issued to Bergius and Sackur in which moist mixes and oxygen under pressure are used.

[2] The manganese dioxide was in the form of commercial pyrolusite containing from 80 to 87 per cent of manganese dioxide in various samples. Each sample was of course analyzed and amounts suitable to produce the desired proportions were taken. The potassium hydroxide was taken from various sources and was also analyzed before use.

[3] This was determined by Sackur's modification of Volhard's method, *Ber.*, **43**, 382.

relationship is a straight line. It is furthermore seen that this line intersects the abscissa representing complete conversion when there are $2^1/_2$ moles of potassium hydroxide for each mole of manganese dioxide. The equation for the reaction given above, which is the one that was accepted before Sackur's work and is the simplest one for the reaction, requires only 2 moles of the alkali. A number of hypotheses might

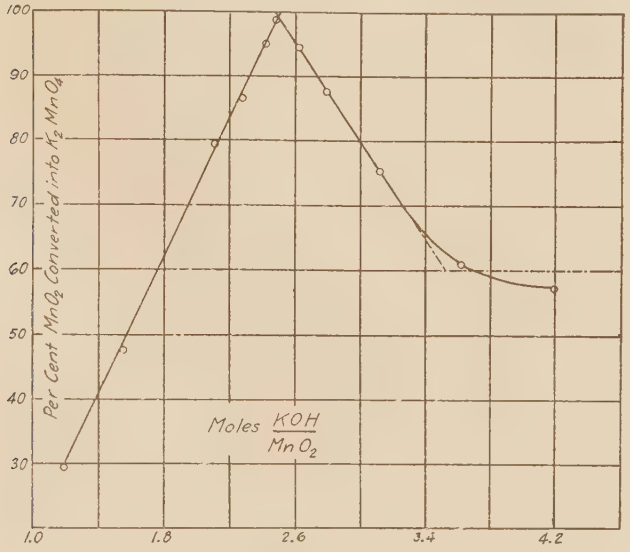

FIG. 1

be advanced in explanation of this phenomenon. In the first place the manganese dioxide used for these experiments was pyrolusite containing about 87 per cent of the dioxide. Some of the impurities like silica are capable of reacting with the caustic, thus decreasing the amount of free alkali in the mix. The same effect would be produced by carbonate originally contained in the caustic and by carbon dioxide absorbed during the unavoidable manipulation of the materials. In this connection it is interesting to note that the amount of alkali, uncombined as potassium manganate, is very nearly half a mole per mole of manganese dioxide in mixes of every composition. Against this hypothesis the following facts must be raised: In the first place, the amount of alkali which would have to be used up by impurities is larger than the impurities contained would be expected to combine with. In the second place, the amount of alkali uncombined as potassium manganate is not quite con-

stant but increases steadily, if slightly, with decrease in total alkali. Finally, the results of Sackur's experiments contradict this view as can be shown by the following: In experiments in which 2.0 moles of alkali were used, every one of pure manganese dioxide, he obtained yields as high as 66 per cent without repulverizing or remoistening the material. We should, therefore, expect that his yields would be low. The curve reproducing our results indicates that for this composition of mix a yield of 72 per cent is to be expected—a value not far from that obtained by Sackur in view of his experimental method. If, on the other hand, we assume that half a mole of the alkali in our experiments is withdrawn from reaction by impurity we should compare Sackur's result with our data for the ratio $1^1/_2$ moles of alkali to one of the dioxide. For this the yield would be only 45.5 per cent. It is seen, therefore, that Sackur's work on pure dioxide agrees quite well with ours on pyrolusite, thus indicating that the impurities in the latter are without great influence. It is, however, not possible to give any adequate explanation for the phenomenon until the work has been repeated at other temperatures in order to ascertain whether the necessity of using an excess of half a mole of the alkali has theoretical significance. At all events, it is certain that Sackur's conclusion that mangani-manganate is the sole product of the treatment of mixes of potassium hydroxide and manganese dioxide in air and that, therefore, the maximum attainable yield is 60 per cent, is incorrect.[1,2,3]

While the curve shows that it is possible to convert

[1] That the products are not mangani-manganates is borne out by their appearance. Mangani-manganates are green; solid manganates are of a very dark violet, almost black hue, not unlike permanganates. All of the products corresponding to the portion of the curve now under discussion had this color. They were free from permanganate.

[2] It is manifest that since excess of alkali is required, the yield can never reach 100 per cent if the amount of alkali used is taken as a basis. The maximum yield on this basis would be 80 per cent since $^1/_2$ mole of excess is required over the 2 moles demanded by the simplest equation. Even this arbitrary way of calculating departs very greatly from the maximum of 60 per cent demanded by Sackur.

[3] It is interesting to consider the possibility presented by the experiments on the effect of moisture cited above. In view of the fact that quite a number of the experiments showed cessation of oxygen absorption when the yield was 60 per cent, one might be led to believe that the mangani-manganates are formed in the absence of moisture and that the catalytic action of water is required to effect their oxidation to manganates. This is not borne out by the one experiment in which in dry air a yield of over 60 per cent was obtained, but it is difficult to exclude the possibility of the presence of water retained in mixes prepared as these are. On the other hand, the dark violet color of the mixes containing an excess of alkali not greater than $^1/_2$ mole indicates that manganates are formed even when the yield is only 60 per cent and that the cessation of oxygen absorption is

all of the manganese into manganate by the use of an excess of very nearly one-half a mole of potassium hydroxide over that required by the simplest equation for the reaction, it also shows very clearly that a larger excess of the hydroxide again lowers the yield. It will be noticed that of the points representing the larger excess of caustic, three lie on a straight line. The fourth point no longer is on this line but corresponds to a yield of very nearly 60 per cent. The fifth point is also fairly close to a 60 per cent yield. Now it is practically impossible to attain equilibrium at the temperature of these experiments (450°) with mixes containing a very large excess of potassium hydroxide because the material becomes soft and sticky and is soon so firmly attached to the walls of the cylinder in which it is heated that its removal for analysis and pulverization in the cylinders are alike impossible. This was particularly noticeable in the experiment in which the ratio was 4.2 moles of the hydroxide to one of the dioxide and the heating had to be interrupted before absorption of oxygen had stopped.[1] Consequently we have indicated by the dotted line the course which the curve would probably take had equilibrium been established in every case.

The interpretation of the curve is simple. Calculation, based on the data presented, shows that between 2 and 3 moles of potassium hydroxide are required beyond the excess of $^1/_2$ mole needed for the complete conversion of manganese dioxide into manganate for the decomposition of one mole of potassium manganate. This corresponds fairly well, though not exactly, with the equation

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due to incomplete mixing of the components before remoistening. Why the cessation of oxygen occurs so often at 60 per cent yield can probably be explained as follows: In the first place, the absorption of oxygen after 60 per cent of the possible amount has been taken up is slow. In the second place, as will be seen from the curve, excess of alkali decomposes the manganate into mangani-manganate. As the alkali is the soluble component, it is likely that certain portions of the dioxide are coated in the drying process with an excess of the alkali and these portions, therefore, are likely to become converted into mangani-manganate. Other portions of the dioxide, therefore, are deficient in alkali and do not get oxidized to a maximum. That the oxidation should appear to stop at 60 per cent is not, after all, very surprising, and we incline at present to the view that this phenomenon is a coincidence and not evidence that water is required to oxidize the mangani-manganates.

[1] It is interesting to note that in the other experiments the data presented represent true equilibrium conditions, inasmuch as the final values have been obtained both by decomposing mixes high in manganate by adding excess of alkali or of manganese dioxide and by starting with potassium hydroxide and manganese dioxide.

$$5K_2MnO_4 + 6KOH \longrightarrow 2K_2MnO_3.3K_2MnO_4.3K_2O + 3H_2O + O_2.$$[1]

It seems that the mangani-manganate described by Sackur is the final product of the reaction when a large excess of alkali is used. It is not, however, the sole product of the reaction as Sackur thought and is not formed unless there is an excess of alkali greater than $^1/_2$ mole. It therefore plays no rôle in the manufacture of manganate by the method discussed in this paper.[2] This conclusion is borne out by the appearance of the mixes after the reaction is complete. The mixes which are deficient in alkali have the dark violet, almost black hue, characteristic of the manganates even though the reaction has gone only half way to completion as, for example, in the experiments in which 1.2 and 1.5 moles of caustic were used per mole of manganese dioxide. On the other hand, those mixes which contain an excess of alkali and which show a similarly low yield have the deep green color of mangani-manganates.[3]

It is self-evident that the results thus obtained are of great practical interest in addition to the purely theoretical interest they possess, for they mean that

[1] Of the 5 mols. of manganate only 2 are decomposed to manganite. Hence 3 moles of KOH are needed according to this equation for one of the manganate.

[2] It must be explicitly stated that the conclusions we have reached refer only to the conditions obtaining at 450°. Many of Sackur's experiments were carried out at nearly 900°. It is possible that at temperatures as high as this manganates decompose into mangani-manganates even without an excess of alkali, since the decomposition temperature of pure potassium manganate in an atmosphere of air is approximately 600°. Sackur would nevertheless not have been justified in applying his deductions to conditions at lower temperatures. The reason why at lower temperatures he was unable to obtain yields corresponding to the formation of manganate is that, as inspection of his data reveals, he used either too little or too much alkali.

[3] There is an apparent contradiction in the statements that potassium hydroxide can decompose the manganate and that at the same time manganate is not formed unless an excess of the hydroxide is present. Thus in the early stages of the treatment there is only a little of the manganate formed and there is, therefore, a large excess of alkali. Or, take for example, the result in the experiment in which the ratio of alkali to dioxide is 1.55 moles of the former to 1.0 of the latter. Here the yield is only 47.5 per cent. The final mix, therefore, contains 0.476 mole of the manganate and 0.6 mole of alkali, or an excess of about 1.2 moles of alkali for each mole of manganate, and it might be thought that this excess ought to decompose the manganate. This contradiction disappears, however, if the very logical assumption be made that the potassium hydroxide and manganese dioxide combine initially to form potassium manganite and that this is subsequently oxidized to the manganate. In this connection it is interesting to note that when the components are first mixed and dried the mass has a green color. When the excess of alkali does not exceed $^1/_2$ mole, this color rapidly changes to that of the true manganates. Apparently then manganate and manganite do not combine to form the double compound postulated except in the presence of excess of alkali.

in order to obtain good yields of manganate in this process the manufacturer must regulate very closely his proportions of manganese ore and caustic, as either a deficiency or an excess of 10 per cent of alkali will lower the yield by 10 to 15 per cent. In the second place the curve shows exactly what yield should be obtained for whatever ratio may be employed for any given mix and will give to the manufacturer a criterion for judging whether recourse to remoistening will be profitable or whether recausticizing of the alkali is necessary.

II—THE INFLUENCE OF IMPURITIES, ESPECIALLY SODIUM, ON THE COURSE OF THE REACTION

While the part of the investigation reported in the first section of this paper makes clear why previous investigators have not succeeded in converting all of the manganese dioxide into manganate, it sheds no light on the question raised by the fact, reported to us by a manufacturer, that new caustic and new manganese dioxide may give very much higher yields than are obtained when the residual and recovered materials are mixed with the new. It is manifest that there can be only two possible causes for the deterioration—either impurities are introduced into the materials in the course of the process or the manganese dioxide must become changed into a less active modification. In order to clear up this point we proceeded, after we had determined what yields might be expected as has been described, to work with the recovered alkali and the residual dioxide. While a few experiments were carried on in which both were used, the yields obtained were so very low that we abandoned this line and attacked the question by working with new manganese dioxide ore and recovered alkali in one set of experiments and with residual manganese dioxide and new caustic in another set.

The first of these two sets of experiments was the one in which new ore and recovered caustic were used to make up the mixes. The caustic was furnished us in the form of a fairly concentrated solution. It was colored green by a small amount of unconverted manganate. After analysis[1] of the solution it was

[1] Before analysis of the solutions, they were freed from manganate by reducing it to manganese dioxide by the addition of a drop or two of formaldehyde solution. After the manganese dioxide had been filtered off, the clear solution could be titrated for free alkali or carbonate by any of the customary methods. The use of formaldehyde, while not entirely free from objection, introduced no error large enough to be of importance for this work.

mixed with enough of the ore to produce a mix of the desired proportions. This was then treated exactly as has been described in the earlier portions of the paper.

The mixes were made up to contain from 2.17 to 2.33 moles of potassium hydroxide to one mole of manganese dioxide—a proportion chosen because it conformed to that used by the manufacturer with whom we were coöperating and from whom we obtained all of the recovered or regenerated materials. Reference to the curve will show that with new caustic and new ore we should have obtained with these proportions yields of about 85 per cent. When we substituted the recovered alkali for the new a very striking lowering of the yield resulted, for we were not able to obtain one better than about 27 to 30 per cent and repeated remoistening and treatment with oxygen even under a pressure of 40 lbs.[1] produced no improvement. There is, therefore, no doubt that these solutions contain some impurity which interferes with the success of the reaction. The foreign substances present in greatest amount were carbonate, chloride, manganate, silicate, and sodium. It was found that the first four named had no appreciable effect on the yield when they were separately added to new materials. Likewise, no other impurities removable by calcium hydroxide could have been responsible for the difficulty, since careful causticization of the liquor did not improve it.[2]

The case was found to be quite different when the effect of sodium was investigated. Analysis of the liquors furnished us showed in different samples that from 25 to 40 per cent of the alkali was in the form of sodium hydroxide. When mixes were made up from new material in which we used pure sodium hydroxide and pure potassium hydroxide in these same proportions the yields resulting were, respectively, 38 and 27 per cent. It was clear at once that here lies the source of the difficulty. In view of the fact that, even if the original caustic contains only a small amount of sodium, the latter is bound to accumulate as the caustic

[1] A series of experiments was conducted to determine the effect of oxygen under pressure (20 to 40 lbs.). So far as we have been able to determine up to the present such treatment merely hastens the oxidation but does not affect the final yield.

[2] The recovered alkali must of course be causticized from time to time since the carbonate is apparently quite inert at the temperatures best employed for the manufacture of manganate. How often this should be done can easily be determined by use of the curve, which shows how great a reduction in yield a given decrease in free alkali will cause.

is used over and over again,[1] it seemed advisable to subject the influence of sodium to a systematic study, the results of which are discussed in the following paragraphs.

For this purpose we made up a series of mixes from the pyrolusite and sodium and potassium hydroxides in which the mole ratio of the alkali to manganese dioxide was kept at 2.28 to 1.0, but in which the proportion of sodium hydroxide was varied in successive experiments from 0 to 100 per cent of the total alkali. The results of this series are reproduced in Table II. In the table the first column contains the amount of sodium hydroxide in the total caustic expressed in weight per cent; the second column, the relative amount of sodium hydroxide in mole per cent; the third column, the per cent by weight of manganate obtained by the first heating in moist air; the fourth column, the per cent of manganate obtained after remoistening and reheating in moist air as previously described; the fifth column, the per cent of manganate obtained when oxygen was passed over the mixes which no longer took up oxygen from air; and the sixth column, the percentage yield determined as already described.[2]

TABLE II—SHOWING THE EFFECT OF SODIUM HYDROXIDE ON THE YIELD OF MANGANATE

Weight Per cent NaOH	Mole Per cent NaOH	MnO_4 in air Per cent	MnO_4 Remoistened Per cent	MnO_4 in O_2 Per cent	Yield Per cent
0.0	0	45.0	45.0	45.9	85.0
19.5	25	33.5	35.6	39.0	71.1
41.5	50	15.8	19.2	26.0	44.0
68.2	75	16.7	15.5	16.7	26.5
100.0	100	15.2	15.0	15.5	23.4

The depressing effect which substitution of sodium for potassium hydroxide exerts on the yield of manganate is strikingly shown by the table. There are two possible hypotheses which may be used to explain the phenomenon. The first is based on the work of Sackur[3] who found that the mangani-manganate which he obtained at high temperatures had the formula

[1] This is due to the fact that sodium permanganate is extremely soluble and that therefore only the potassium is removed when the permanganate is crystallized out.

[2] The reader must note that the percentages given in the third, fourth, and fifth columns refer to per cent by weight of MnO_4 and not to the amount of the sodium or the potassium salt. We have made this change because in those cases in which both sodium and potassium hydroxide are used, both the sodium and the potassium salt are probably formed. The relative amount of the two is not known and therefore the method of expressing the results here used is the only one free from objection.

[3] *Ber.*, **44** (1911), 777.

$Na_2MnO_3.Na_2MnO_4.2Na_2O$

and therefore represents a lower stage of oxidation than does the potassium mangani-manganate of the formula $2K_2MnO_3.3K_2MnO_4.3K_2O$. We have shown, however, that at the temperatures used in this investigation, as well as in practice, the manganate and not the mangani-manganate is formed when potassium hydroxide alone is used. If the explanation based on Sackur's interpretation of the reaction is to be used, we must assume that sodium manganate is much less stable than is the corresponding potassium salt. This assumption is not borne out by some preliminary experiments made by us on a fairly pure sample of sodium manganate prepared from sodium permanganate according to the directions of Auger.[1] Our experiments indicate that sodium manganate is fairly stable unless an excess of sodium hydroxide is present, under which conditions the sodium salt, like the potassium salt, decomposes into the mangani-manganate. It seems much more likely, then, that the behavior of mixtures of sodium hydroxide and manganese dioxide will prove to be similar to that of mixtures of potassium hydroxide with the dioxide. It is, therefore, quite possible that the peak in the curve for sodium hydroxide might correspond to a different composition than for potassium hydroxide, or that the angle at the peak is a much smaller one.[2] The final interpretation must await the completion of experiments on sodium manganate which will be reported in a later paper.

III—DETERIORATION OF THE RESIDUAL MANGANESE DIOXIDE AND VARIATIONS IN THE BEHAVIOR IN MANGANESE DIOXIDE FROM VARIOUS SOURCES

Although we have shown in the preceding section of this paper one of the causes of the decrease in the efficiency of the process when recovered material is used, there is still the possibility that the recovered manganese dioxide also may not be as satisfactory as the new ore. Manufacturers agree that ores from various sources may differ greatly in the ease and completeness with which they can be converted into man-

[1] *Compt. rend.*, **151** (1910), 69.

[2] The only indications we have at the present as to whether the ratio, 2.28 moles of sodium hydroxide to 1.0 of manganese dioxide, lies on the upward or downward portion of the curve if such a curve exists, are contradictory. On the one hand a single experiment in which we used a larger amount of sodium hydroxide gave a considerably higher yield, but on the other hand the final mixes of the composition given above are green in color, whereas sodium manganate like potassium manganate is of a very dark violet hue.

ganate although they may contain equal amounts of manganese dioxide. In this connection one of our experiences is of interest. A second series like that described in the second section of this paper was performed with a different ore containing approximately the same amount of manganese dioxide. The results of the two series are compared in Table III in which the first row gives the mole per cent of the total alkali present as sodium hydroxide, the second row the final yield obtained with the first ore, and the third row the final yield obtained with the second ore.

TABLE III—SHOWING THE BEHAVIOR OF DIFFERENT ORES

Mole per cent NaOH.....	0	25	50	75	100
Yield with first ore, per cent.....	85.0	71.1	44.00	26.5	23.4
Yield with second ore, per cent.....	56.3	53.7	39.0	25.6	21.5

It is seen that the second ore gave very much lower yields when the alkali was all in the form of potassium hydroxide and that the difference becomes smaller as more sodium is introduced. After many ineffectual efforts to improve the yield with the second ore we finally found that if it was remoistened more than once as described in the first section of the paper the yield for the mixture with no sodium was raised to the same value as was obtained with the first ore. By this time, however, the mixes had been rotated for many hours in the kilns and had, therefore, become thoroughly pulverized. When we, therefore, ground the ore very fine before using it the results were likewise improved. The state of division is not, however, the sole factor in the difference between the two ores for we have worked with ore coarser than the second and obtained excellent results. A more important factor appears to be the ease with which the ore becomes pulverized in the kilns (hardness).

In view of the facts stated, we therefore made another set of experiments in which we used recovered and residual manganese dioxide with new potassium hydroxide. The former was obtained from the same manufacturer who had furnished us with the recovered alkali described in the second section. The ratio of alkali to manganese dioxide was again 2.28 moles of the former to one of the latter. When the old manganese dioxide, as we may call the material for brevity, was used just as it was received, it gave uniformly low yields—from 25 per cent to 35 per cent of the theoretical—while we should have obtained about 85 per cent. Since it is well known that manganese dioxide absorbs (or perhaps combines with)

relatively large amounts of caustic alkalies, we suspected that the old dioxide might be contaminated with considerable sodium hydroxide. We therefore washed it very thoroughly with water and in some cases boiled it with dilute nitric acid. When the recovered and residual dioxide was fresh it responded very well to this treatment; material which had been kept for some time, and especially material which had dried out, was not much improved. These results point to the conclusion that it was the absorbed sodium hydroxide which was responsible for the deteriorating of the dioxide and which becomes more difficult to remove as the material dries out. Since the first section of the paper shows how large amounts of residual dioxide can be avoided and as it is not necessary to convert the manganate into permanganate by processes in which large amounts of dioxide are reprecipitated, it did not seem necessary for us to follow up this point further.

SUMMARY

1—It is found that when manganese dioxide is heated with potassium hydroxide in a current of air to produce potassium manganate, the reaction frequently stops before the maximum oxidation stage has been reached. This can be avoided by remoistening and reheating the mix; the use of moistened air also is helpful.

2—The yield of potassium manganate varies greatly with the proportion of potassium hydroxide in the mixes. At the temperatures at which these experiments were carried out and with the pyrolusite used, practically all of the manganese dioxide is converted into manganate when 2.5 moles of potassium hydroxide are used for each mole of manganese dioxide.

3—The conclusions of Sackur that in this reaction mangani-manganates and not manganates are obtained and that the maximum yield attainable is, therefore, only 60 per cent, is thus proved to be incorrect.

4—Larger amounts of alkali, however, cause the manganate to decompose into a mangani-manganate, similar to, if not identical with, that postulated by Sackur.

5—The substitution of sodium hydroxide for potassium hydroxide greatly lowers the yield if the proportions between alkali and manganese dioxide named are employed. What the effect of other proportions would be is as yet undetermined. Care must be taken,

therefore, not to allow sodium to accumulate in the recovered caustic when the operation is carried out continuously.

6—It is very important to pulverize the ores very finely and to keep them finely divided in the kilns in order to obtain the highest possible yields. Some ores are more difficult to handle in this respect than are others.

7—The residual manganese dioxide sometimes deteriorates on repeated use. This may be caused by absorption of impurities from the solution. If the dioxide before it has had time to dry out is thoroughly washed with water or boiled with dilute nitric acid, its effectiveness for the process may be restored.

In closing I wish to acknowledge the aid and encouragement given me by Professor Schlesinger in carrying out this investigation and the coöperation of Mr. R. D. Mullinix in the experimental work.